(54) Title: REDUCTION OF AMMONIA WASTES ASSOCIATED WITH AMMOXIDATION PROCESSES

(57) Abstract

Ammonia effluent from fluid bed processes for catalytic ammoxidation of propylene to form acrylonitrile are reduced by introduction of methanol into the fluid bed at selected locations.

REDUCTION OF AMMONIA WASTES
ASSOCIATED WITH AMMOXIDATION PROCESSES

BACKGROUND OF THE INVENTION

This application is a continuation-in-part of

5   United States patent application serial number
08/390,726 filed February 17, 1995 and copending
herewith.

The invention relates to reduction of ammonia
wastes produced in processes for production of

10 acrylonitrile by catalytic ammoxidation of propylene in
a fluidized bed reaction.

Commercial processes for production of
acrylonitrile by passage of propylene, oxygen (air),
and ammonia through a fluidized bed of ammoxidation

15 catalyst are well known by those skilled in the art.
In such processes an excess of ammonia is commonly
employed and necessary to obtain high levels of
conversion of propylene to acrylonitrile. As a result,
significant levels of ammonia are present in the

20 product stream and must be recovered and/or converted
to other waste products such as ammonium nitrates or
sulfates at considerable expense.

The addition of methanol to processes of
catalytic ammoxidation of propylene to acrylonitrile in

25 order to increase hydrogen cyanide co-product
production and, to some extent, consume excess ammonia
is known. It is further known that methanol can
compete with propylene in ammoxidation reactions and
difficulty may be experienced in preventing reduction

30 in acrylonitrile yields.

It will be appreciated by those skilled in
the art that processes for reducing ammonia wastes
without seriously impairing conversion of propylene to
acrylonitrile are desired from the standpoint of both

35 economic and environmental considerations.

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SUMMARY OF THE INVENTION

The invention is based on the discovery that in a process for making acrylonitrile by passing propylene, oxygen (air), and ammonia through a

5   fluidized bed of ammoxidation catalyst, the amount of ammonia contained in the product stream can be effectively and economically reduced without substantial adverse effect on acrylonitrile yield by introducing methanol into the reactor under non-coking

10   conditions at a point and in an amount such that ammonia in the reactor effluent is substantially reduced without undue reduction in acrylonitrile yield. This continuation is particularly directed to the prevention of blockage of the methanol addition means

15   used in the process. The invention will be fully understood from the following description of the preferred embodiments.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with this invention, methanol

20   is introduced into a fluidized bed reaction system in which a bed of ammoxidation catalyst is fluidized by a flow of the reactants, propylene, ammonia, and oxygen containing gas (air). The use of such systems for the manufacture of acrylonitrile is well known.

25   Essentially any of the numerous catalysts known for the ammoxidation of propylene can be employed using conventional ammoxidation reaction conditions. For example, catalysts mainly consisting of bismuth phosphates or molybdates or of antimony and uranium

30   oxides or of bismuth phosphates or molybdates doped with iron, nickel, cobalt etc., or of antimony oxide and oxides of metals such as iron, cobalt, or nickel may be used. A particularly preferred catalyst is represented by the formula $Sb_aU_bFe_cBi_dMo_eMe_fO_g$ in which Me

35   is nickel or cobalt, a is 1 to 10, b is 0.1 to 5, c is 0.1 to 5, d is 0.001 to 0.1, e is 0.001 to .1, f is 0

to 0.1 and g is a number taken to satisfy the valences
of the quantities of other components present.
Ammoxidation processes using catalysts of this type are
described, for example, in U.S. Patents 4,018,712,

5   4,545,943, and 4,487,850, the disclosures of these
patents being incorporated herein by reference.

The methanol will be introduced at a point
and in an amount such that the ammonia content of the
reactor effluent will be less than 0.5 mole percent and

10   lower than if no methanol were introduced and such that
acrylonitrile production measured as weight per unit of
time is at least 97% by weight of what would be
obtained if no methanol were introduced. Preferably,
ammonia effluent will be less than 0.25 mole percent

15   or, most preferably, substantially eliminated with less
than 1% reduction in acrylonitrile production.

In a preferred embodiment of the invention,
the methanol is introduced into the fluidized bed
reactor at a point where 5% to 60% by weight of the

20   catalyst in the reactor is above the methanol
introduction point. Such point can be determined by
calculational methods well understood by those skilled
in the fluid bed art or by actual measurement
techniques based, for example, on pressure measurements

25   made at various reactor heights. The weight of the
catalyst above the injection point refers to the weight
when the bed is fluidized under operating conditions.
Also, it is contemplated that the catalyst charge will
be an amount chosen to ensure complete ammoxidation of

30   the propylene but without undue excess. The optimum
point of introduction may vary depending on how much
excess catalyst, if any, is present; catalyst activity;
surface area; etc. For any system, the optimum
injection point can be determined by routine testing

35   conducted in light of the disclosure herein.

The amount of methanol used will be
sufficient to react with a major portion of the ammonia

not reacted with propylene. However it is desirable to
avoid excesses of methanol which would be expensive to
separate from the acrylonitrile product. Preferably,
the methanol content of the effluent will be less than

5   0.25 mole percent, most preferably, less than 0.01 mole
percent. Generally, the use of from 0.8 to 2.0 times
the moles stoichiometrically required to react with the
ammonia in excess of that required for the ammoxidation
of propylene will give satisfactory results.

10   Like the optimum point of methanol
introduction, the amount of methanol to be utilized
will depend upon the catalyst in use and the amount
present; the quantities of other reactants present; and
flow rates in the fluidized bed system. It is

15   preferred to introduce the methanol in a downward
direction so that the openings through which it is
introduced will not become clogged when the reactor is
shut down or methanol flow is stopped for maintenance
or other reasons.

20   Since the methanol introduction means will
generally be of relatively small dimensions and, more
importantly, may not be operated continuously, care
should be taken to prevent blockage. It is
particularly preferred, in order to prevent clogging or

25   blockage in the sparger, tube, or other means through
which methanol is introduced, that a gas flow in
addition to methanol be maintained at all times that a
catalyst charge is present on the reactor, even if the
reactor bed is not fluidized. The gas can be any inert

30   gas which is defined as a gas which will not adversely
affect the reaction or reactor materials of
construction. For example, nitrogen or carbon dioxide
can generally be used at any time. Air can be used in
amounts which will not form explosive mixtures with

35   methanol (or in any amount if the reactor is "down" or
if methanol is not being introduced into the reaction).
Steam can be conveniently and advantageously used if

the reaction is in progress. Mixtures of gases can be
used.   The gas flow linear velocity through the
orifices of the methanol introduction means should
exceed (preferably by ten to fifty times) the linear
5   velocity of other gases through the fluid bed reactor.
If the reactor is "down" and no gas flow, for example,
from purges of the reactant inlets, is present, it is
still desirable to maintain a minimal flow to ensure
catalyst fines are not drawn into the methanol
10   introduction means. It is further desirable that the
openings in the sparger, tube, or other means through
which methanol is introduced be significantly larger
than the catalyst particles present in the reactor.
More specifically, the diameters of the openings (or
15   smallest dimension of the opening if non-round openings
are used) should be at least ten, preferably, at least
twenty or thirty times the mean particle size of the
largest 10% by weight of the catalyst particles. There
is no upper limit on opening size except such as may be
20   dictated by considerations of gas flow patterns and
rates which may also render it desirable to decrease
the number of openings as opening size increases.

It is known that methanol in contact with
iron or iron containing alloys or materials of
25   construction will undergo reactions leading to coking
at elevated temperatures such as commonly employed in
ammoxidation reactions. In order to minimize down time
for cleaning coked reactor inlet lines and spargers, it
is important that the methanol be introduced under non-
30   coking conditions. This can be accomplished by use of
non-ferrous or high molybdate containing stainless
steel inlet lines and spargers, but the expense may be
undesirable. Alternatively, the portion of the inlet
line between the reactor inlet point and point of
35   discharge can be insulated to maintain the temperature
of the conduit below coking temperature but this is
frequently inconvenient and the space occupied inside

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the reactor by an insulated conduit may interfere with fluid bed flow patterns. In accordance with the present invention, it is preferred to prevent major coking by vaporizing the methanol prior to the point

5   the methanol inlet line enters the reactor and by locating the inlet line entry point as close to its point of discharge (the sparger) inside the reactor as possible.

In order to prevent coking, it is

10   particularly preferred to mix the methanol with water vapor (steam) and/or air. Steam is preferred in order to prevent the possible formation of combustible or explosive mixtures. Coking can generally be adequately prevented by the use of a mixture of methanol with at

15   least 20 mole percent steam or air or mixture thereof. The use of additional steam or air (or other gas which does not adversely affect the reaction system) may be desirable to provide a volume of gas flow sufficient to assure good distribution of the methanol in the fluid

20   bed system. However, the amount of air, if any, mixed with the methanol should not be so great as to form a flammable mixture.

Minor modifications in the primary acrylonitrile process may be desirable to optimize

25   production of acrylonitrile and, if desired, co-products such as hydrogen cyanide. Better hydrogen cyanide yields and less loss of acrylonitrile are experienced if the oxygen (air) to propylene ratio is increased so that the oxygen exiting the reaction is

30   about the same as in the case of the conventional (no methanol present) process for ammoxidation of propylene. The oxygen (air) should be sufficient to prevent catalyst reduction but not so great as to form explosive mixtures.

35   The practice of the invention and its comparison with conventional processes is further illustrated by the following examples.

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EXAMPLES I-XVII

In these examples, a 4.1 cm inside diameter
by 1.8 meter high fluidized bed reactor constructed of
316 stainless steel is used. The outlet end of the

5   reactor is connected to a gas chromatograph for
analysis of effluent gases. Propylene, ammonia and air
feeds are supplied via mass flow controllers and are
premixed before being brought into contact with the
fluidized bed. The methanol is fed separately by a

10   positive displacement pump and is vaporized by heating
prior to being introduced into the reactor. The
reactor contains the amount shown in Table 1 below of
catalyst indicated. Catalyst number 1 has the
following composition:
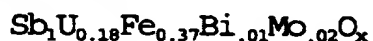
15                       $Sb_1U_{0.18}Fe_{0.37}Bi_{.01}Mo_{.02}O_x$
(O_x indicates the elements are present as their oxides
and the composition contains sufficient oxygen to
satisfy their valences) which is deposited on 50% by
weight SiO_2 carrier. Catalyst 2 is a mixture of iron

20   and antimony oxides deposited on a silica carrier.
Catalyst 3 is a mixture of bismuth, molybdenum, and
iron oxides on a silica carrier.

Since catalyst activity may vary somewhat
with extended usage, each example compares a limited

25   number of successive runs with methanol in the feed
stream against a control in which no methanol is
introduced.

In all cases, an inert gas flow through the
methanol sparger openings (which are about thirty times

30   the diameter of the mean particle size of the largest
10% by weight of the catalyst particles) at a linear
velocity about 30 times greater than the linear
velocity of the flow of other gases through the reactor
is maintained. No clogging of the sparger is observed.

35   No coking is observed in the examples.

TABLE 1

		Example I		Example II	
CATALYST:		1	1	1	1
REACTOR CONDITIONS :					
REACTOR TEMP	deg C	458	458	459	459
REACTOR PRESS	atms	2.02	2.02	2.02	2.01
METHANOL INJ POINT	cms	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		3.91		3.91
CATALYST CHARGE	gms	340	340	340	340
REACTOR FEEDS :					
NH3 FEED	MOL/HR	1.427	1.427	1.419	1.419
C3H6 FEED	MOL/HR	1.299	1.299	1.299	1.299
AIR FEED	MOL/HR	14.25	14.249	14.243	14.243
N2 FEED (w/MeOH)	MOL/HR	0.387	0.387	0.387	0.387
METHANOL FEED	MOL/HR		0.193		0.152
NH3/C3H6 FEED	RATIO	1.098	1.098	1.092	1.092
AIR/C3H6 FEED	RATIO	10.967	10.966	10.961	10.961
MeOH/C3H6 FEED	RATIO		0.148		0.117
EFFLUENT CONDITIONS :					
MOLE % NH3 in EFFLUENT		0.558	0.156	0.450	0.274
MOLE % O2 in EFFLUENT		3.056	2.640	3.334	3.231
MOLES METHANOL OUT			0.085		0.091
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			1.90		1.85
PROPYLENE CONVERSION	mole %	98.751	98.207	98.487	97.904
METHANOL CONVERSION	mole %		56.171		40.253
PRODUCT RESULTS and RESULTS :					
AN MAKE	gms/hr	56.378	56.810	56.444	57.327
HCN MAKE	gms/hr	6.891	7.198	6.481	7.238
RATIO HCN /AN	gms HCN/gm AN	0.122	0.127	0.114	0.126
NH3 Breakthrough	gms/hr	1.729	0.492	1.393	0.861
NH3 Reduction	gms/hr		1.237		0.532

TABLE 1

		Example III		Example IV	
CATALYST:		1	1	1	1
REACTOR CONDITIONS :					
REACTOR TEMP	deg C	459	459	457	457
REACTOR PRESS	atms	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	33.02	33.02
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		3.91		24.29
CATALYST CHARGE	gms	340	340	340	340
REACTOR FEEDS :					
NH3 FEED	MOL/HR	1.418	1.418	1.423	1.423
C3H6 FEED	MOL/HR	1.299	1.299	1.304	1.305
AIR FEED	MOL/HR	14.242	14.243	14.24	14.244
N2 FEED (w/MeOH)	MOL/HR	0.387	0.387	0.387	0.387
METHANOL FEED	MOL/HR		0.152		0.169
NH3/C3H6 FEED	RATIO	1.091	1.091	1.091	1.090
AIR/C3H6 FEED	RATIO	10.961	10.961	10.917	10.912
MeOH/C3H6 FEED	RATIO		0.117		0.130
EFFLUENT CONDITIONS :					
MOLE % NH3 in EFFLUENT		0.422	0.143	0.474	0.112
MOLE % O2 in EFFLUENT		3.306	2.988	3.132	2.377
MOLES METHANOL OUT			0.040		0.017
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			1.98		1.96
PROPYLENE CONVERSION	mole %	98.265	97.452	98.284	97.243
METHANOL CONVERSION	mole %		73.824		89.740
PRODUCT RESULTS and RESULTS :					
AN MAKE	gms/hr	57.442	57.316	55.894	55.184
HCN MAKE	gms/hr	6.472	7.887	6.831	8.720
RATIO HCN /AN	gms HCN/gm AN	0.113	0.138	0.123	0.158
NH3 Breakthrough	gms/hr	1.306	0.449	1.469	0.353
NH3 Reduction	gms/hr		0.857		1.116

TABLE 1

		Example V	
CATALYST:		1	1

REACTOR CONDITIONS :

REACTOR TEMP	deg C	457	458
REACTOR PRESS	atms	2.02	2.01
METHANOL INJ POINT	cms	33.02	33.02
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		24.29
CATALYST CHARGE	gms	340	340

REACTOR FEEDS :

NH3 FEED	MOL/HR	1.422	1.422
C3H6 FEED	MOL/HR	1.304	1.304
AIR FEED	MOL/HR	14.239	14.24
N2 FEED (w/MeOH)	MOL/HR	0.387	0.387
METHANOL FEED	MOL/HR		0.169
NH3/C3H6 FEED	RATIO	1.090	1.090
AIR/C3H6 FEED	RATIO	10.916	10.917
MeOH/C3H6 FEED	RATIO		0.130

EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT		0.488	0.119
MOLE % O2 in EFFLUENT		2.926	2.247
MOLES METHANOL OUT			0.009
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			1.91
PROPYLENE CONVERSION	mole %	98.484	97.596
METHANOL CONVERSION	mole %		94.886

PRODUCT RESULTS and RESULTS :

AN MAKE	gms/hr	55.280	54.459
HCN MAKE	gms/hr	6.961	8.703
RATIO HCN /AN	gms HCN/gm AN	0.126	0.160
NH3 Breakthrough	gms/hr	1.513	0.375
NH3 Reduction	gms/hr		1.138

TABLE 1

		Example VI				

CATALYST:

CATALYST:	1	1	1	1	1

REACTOR CONDITIONS :

REACTOR TEMP	deg C	457	457	457	457	456
REACTOR PRESS	atms	2.02	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		25.75	25.75	25.75	25.75
CATALYST CHARGE	gms	440	440	440	440	440

REACTOR FEEDS :

NH3 FEED	MOL/HR	1.427	1.428	1.427	1.427	1.427
C3H6 FEED	MOL/HR	1.299	1.300	1.300	1.300	1.300
AIR FEED	MOL/HR	14.248	14.249	14.248	14.248	14.246
N2 FEED (w/MeOH)	MOL/HR	0.387	0.387	0.387	0.387	0.387
METHANOL FEED	MOL/HR		0.199	0.150	0.093	0.249
NH3/C3H6 FEED	RATIO	1.098	1.098	1.097	1.097	1.097
AIR/C3H6 FEED	RATIO	10.965	10.958	10.957	10.957	10.955
MeOH/C3H6 FEED	RATIO		0.153	0.115	0.071	0.192

EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT		0.558	0.128	0.133	0.250	0.020
MOLE % O2 in EFFLUENT		2.185	1.403	1.556	1.731	1.120
MOLES METHANOL OUT			0.002	0.001	0.001	0.003
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			1.95	1.47	0.91	2.45
PROPYLENE CONVERSION	mole %	100.000	99.716	99.607	99.795	99.427
METHANOL CONVERSION	mole %		99.229	99.237	99.292	98.814

PRODUCT RESULTS and RESULTS :

AN MAKE	gms/hr	55.312	55.996	54.722	55.274	50.092
HCN MAKE	gms/hr	7.229	8.930	8.859	8.503	8.840
RATIO HCN /AN	gms HCN/gm AN	0.131	0.159	0.162	0.154	0.176
NH3 Breakthrough	gms/hr	1.734	0.406	0.419	0.784	0.064
NH3 Reduction	gms/hr		1.328	1.315	0.950	1.670

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TABLE 1

		Example VII		
CATALYST:		1	1	1

REACTOR CONDITIONS :

REACTOR TEMP	deg C	461	461	461
REACTOR PRESS	atms	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		14.03	14.03
CATALYST CHARGE	gms	380	380	380

REACTOR FEEDS :

NH3 FEED	MOL/HR	1.425	1.426	1.425
C3H6 FEED	MOL/HR	1.299	1.299	1.299
AIR FEED	MOL/HR	14.258	14.257	14.259
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.159	0.319
NH3/C3H6 FEED	RATIO	1.097	1.098	1.097
AIR/C3H6 FEED	RATIO	10.977	10.976	10.978
MeOH/C3H6 FEED	RATIO		0.122	0.245

EFFLUENT CONDITIONS :

MOLE % NH3 In EFFLUENT		0.819	0.310	0.037
MOLE % O2 In EFFLUENT		3.645	2.933	2.317
MOLES METHANOL OUT			0.012	0.042
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			1.07	2.14
PROPYLENE CONVERSION	mole %	98.705	98.249	97.855
METHANOL CONVERSION	mole %		92.411	86.732

PRODUCT RESULTS and RESULTS :

AN MAKE	gms/hr	54.790	53.652	53.895
HCN MAKE	gms/hr	7.307	10.126	10.936
RATIO HCN /AN	gms HCN/gm AN	0.133	0.189	0.203
NH3 Breakthrough	gms/hr	2.541	0.977	0.118
NH3 Reduction	gms/hr		1.564	2.423

TABLE 1

		Example VIII			Example IX	
CATALYST:		1	1	1	1	1
REACTOR CONDITIONS :						
REACTOR TEMP	deg C	461	462	461	461	460
REACTOR PRESS	atms	2.02	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		14.03	14.03		18.33
CATALYST CHARGE	gms	380	380	380	400	400
REACTOR FEEDS :						
NH3 FEED	MOL/HR	1.425	1.425	1.425	1.425	1.425
C3H6 FEED	MOL/HR	1.299	1.299	1.299	1.299	1.299
AIR FEED	MOL/HR	14.258	14.257	14.506	14.266	14.269
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.317	0.317		0.222
NH3/C3H6 FEED	RATIO	1.097	1.097	1.097	1.099	1.099
AIR/C3H6 FEED	RATIO	10.977	10.976	11.168	10.983	10.986
MeOH/C3H6 FEED	RATIO		0.244	0.244		0.171
EFFLUENT CONDITIONS :						
MOLE % NH3 in EFFLUENT		0.798	0.000	0.000	0.808	0.120
MOLE % O2 in EFFLUENT		3.442	2.047	2.514	2.904	2.042
MOLES METHANOL OUT			0.102	0.101		0.014
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			2.18	2.18		2.00
PROPYLENE CONVERSION	mole %	99.027	98.128	97.790	99.068	98.522
METHANOL CONVERSION	mole %		67.946	68.104		93.548
PRODUCT RESULTS and RESULTS :						
AN MAKE	gms/hr	54.496	54.158	54.079	54.783	54.166
HCN MAKE	gms/hr	7.518	10.070	10.146	7.518	9.858
RATIO HCN /AN	gms HCN/gm AN	0.138	0.186	0.188	0.137	0.182
NH3 Breakthrough	gms/hr	2.477	0.000	0.000	1.889	0.381
NH3 Reduction	gms/hr		2.477	2.477		1.508

TABLE 1

		Example X			Example XI	
CATALYST:		1	1	1	1	1
REACTOR CONDITIONS :						
REACTOR TEMP	deg C	460	461	461	460	461
REACTOR PRESS	atms	2.02	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MaOH INJECTION PT.	%		18.33	18.33		18.33
CATALYST CHARGE	gms	400	400	400	400	400
REACTOR FEEDS :						
NH3 FEED	MOL/HR	1.428	1.427	1.428	1.427	1.427
C3H6 FEED	MOL/HR	1.299	1.299	1.299	1.299	1.300
AIR FEED	MOL/HR	14.283	14.281	14.318	14.528	14.537
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.278	0.333		0.333
NH3/C3H6 FEED	RATIO	1.099	1.099	1.099	1.099	1.098
AIR/C3H6 FEED	RATIO	10.983	10.980	11.023	11.184	11.183
MeOH/C3H6 FEED	RATIO		0.214	0.257		0.255
EFFLUENT CONDITIONS :						
MOLE % NH3 in EFFLUENT		0.544	0.020	0.020	0.559	0.017
MOLE % O2 in EFFLUENT		2.850	1.761	1.431	2.954	1.594
MOLES METHANOL OUT			0.034	0.000		0.034
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			2.80	3.36		3.22
PROPYLENE CONVERSION	mole %	99.349	98.457	98.034	99.475	98.271
METHANOL CONVERSION	mole %		87.814	100.000		89.923
PRODUCT RESULTS and RESULTS :						
AN MAKE	gms/hr	55.338	55.762	54.818	54.808	54.545
HCN MAKE	gms/hr	7.414	9.648	10.948	7.512	10.129
RATIO HCN /AN	gms HCN/gm AN	0.134	0.173	0.200	0.137	0.186
NH3 Breakthrough	gms/hr	1.690	0.064	0.064	1.762	0.055
NH3 Reduction	gms/hr		1.626	1.626		1.707

TABLE 1

		Example XII		Example XIII		
CATALYST:		2	2	3	3	3

REACTOR CONDITIONS :

REACTOR TEMP	deg C	451	449	460	459	459
REACTOR PRESS	atms	2.02	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		43.88		26.52	26.52
CATALYST CHARGE	gms	650	650	578	578	578

REACTOR FEEDS :

NH3 FEED	MOL/HR	1.359	1.360	1.562	1.562	1.562
C3H6 FEED	MOL/HR	1.299	1.299	1.299	1.299	1.299
AIR FEED	MOL/HR	15.659	15.658	13.312	13.311	13.769
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.278		0.139	0.139
NH3/C3H6 FEED	RATIO	1.046	1.047	1.203	1.203	1.203
AIR/C3H6 FEED	RATIO	12.056	12.055	10.249	10.248	10.601
MeOH/C3H6 FEED	RATIO		0.214		0.107	0.107

EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT		0.577	0.102	0.420	0.140	0.123
MOLE % O2 in EFFLUENT		3.810	2.508	1.242	0.963	1.354
MOLES METHANOL OUT			0.025		0.010	0.023
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			2.47		1.89	1.89
PROPYLENE CONVERSION	mole %	98.042	97.109	99.021	98.866	98.782
METHANOL CONVERSION	mole %		90.912		92.967	83.701

PRODUCT RESULTS and RESULTS :

AN MAKE	gms/hr	54.343	54.198	51.056	50.795	50.515
HCN MAKE	gms/hr	5.820	8.699	9.831	11.364	11.247
RATIO HCN /AN	gms HCN/gm AN	0.107	0.161	0.193	0.224	0.223
NH3 Breakthrough	gms/hr	1.915	0.347	1.249	0.422	0.380
NH3 Reduction	gms/hr		1.568		0.827	0.868

TABLE 1

		Example XIV		Example XV	
CATALYST:		3	3	1	1
REACTOR CONDITIONS :					
REACTOR TEMP	deg C	459	458	460	460
REACTOR PRESS	atms	2.02	2.02	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		28.52		12.88
CATALYST CHARGE	gms	578	578	375	375
REACTOR FEEDS :					
NH3 FEED	MOL/HR	1.562	1.561	1.425	1.426
C3H6 FEED	MOL/HR	1.299	1.299	1.299	1.299
AIR FEED	MOL/HR	13.772	14.122	14.249	14.25
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.251		0.139
NH3/C3H6 FEED	RATIO	1.203	1.202	1.097	1.098
AIR/C3H6 FEED	RATIO	10.603	10.873	10.970	10.971
MeOH/C3H6 FEED	RATIO		0.193		0.107
EFFLUENT CONDITIONS :					
MOLE % NH3 in EFFLUENT		0.400	0.000	0.412	0.091
MOLE % O2 in EFFLUENT		1.742	1.311	2.965	2.471
MOLES METHANOL OUT			0.033		0.012
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			3.50		1.85
PROPYLENE CONVERSION	mole %	99.022	97.927	99.182	98.766
METHANOL CONVERSION	mole %		86.828		91.675
PRODUCT RESULTS and RESULTS :					
AN MAKE	gms/hr	50.627	50.695	55.052	54.489
HCN MAKE	gms/hr	10.081	12.155	7.320	9.655
RATIO HCN /AN	gms HCN/gm AN	0.199	0.240	0.133	0.177
NH3 Breakthrough	gms/hr	1.222	0.000	1.278	0.288
NH3 Reduction	gms/hr		1.222		0.992

TABLE 1

		Example XVI	
CATALYST:		1	1
REACTOR CONDITIONS :			
REACTOR TEMP	deg C	464	463
REACTOR PRESS	atms	2.02	2.02
METHANOL INJ POINT	cms	41.91	41.91
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		12.88
CATALYST CHARGE	gms	375	375
REACTOR FEEDS :			
NH3 FEED	MOL/HR	1.426	1.426
C3H6 FEED	MOL/HR	1.299	1.299
AIR FEED	MOL/HR	14.248	14.25
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374
METHANOL FEED	MOL/HR		0.195
NH3/C3H6 FEED	RATIO	1.098	1.098
AIR/C3H6 FEED	RATIO	10.970	10.971
MeOH/C3H6 FEED	RATIO		0.150
EFFLUENT CONDITIONS :			
MOLE % NH3 in EFFLUENT		0.403	0.009
MOLE % O2 in EFFLUENT		3.027	2.204
MOLES METHANOL OUT			0.026
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			2.65
PROPYLENE CONVERSION	mole %	99.196	98.415
METHANOL CONVERSION	mole %		86.517
PRODUCT RESULTS and RESULTS :			
AN MAKE	gms/hr	54.223	54.047
HCN MAKE	gms/hr	7.187	9.471
RATIO HCN /AN	gms HCN/gm AN	0.133	0.175
NH3 Breakthrough	gms/hr	1.250	0.028
NH3 Reduction	gms/hr		1.222

TABLE 1

Example XVII

CATALYST:		1	1	1	1

REACTOR CONDITIONS :

REACTOR TEMP	deg C	462	461	461	460
REACTOR PRESS	atms	2.01	2.01	2.01	2.01
METHANOL INJ POINT	cms	0.00	0.00	0.00	0.00
WT % of CATALYST ABOVE the MeOH INJECTION PT.	%		100.00	100.00	100.00
CATALYST CHARGE	gms	400	400	400	400

REACTOR FEEDS :

NH3 FEED	MOL/HR	1.426	1.652	1.702	1.717
C3H6 FEED	MOL/HR	1.299	1.299	1.299	1.299
AIR FEED	MOL/HR	14.25	16.509	16.76	16.766
N2 FEED (w/MeOH)	MOL/HR	0.374	0.374	0.374	0.374
METHANOL FEED	MOL/HR		0.503	0.503	0.503
NH3/C3H6 FEED	RATIO	1.098	1.272	1.310	1.322
AIR/C3H6 FEED	RATIO	10.971	12.710	12.904	12.906
MeOH/C3H6 FEED	RATIO		0.387	0.387	0.387

EFFLUENT CONDITIONS :

MOLE % NH3 in EFFLUENT		0.451	0.266	0.387	0.437
MOLE % O2 in EFFLUENT		3.202	2.955	3.225	3.153
MOLES METHANOL OUT			0.006	0.006	0.006
MOLES MeOH FEED /MOLE NH3 IN BC EFFLUENT			6.12	6.12	6.12
PROPYLENE CONVERSION	mole %	99.084	96.848	96.813	96.943
METHANOL CONVERSION	mole %		98.900	98.889	98.888

PRODUCT RESULTS and RESULTS :

AN MAKE	gms/hr	55.639	54.078	54.626	54.585
HCN MAKE	gms/hr	6.943	15.262	15.625	15.629
RATIO HCN /AN	gms HCN/gm AN	0.125	0.282	0.286	0.286
NH3 Breakthrough	gms/hr	1.398	0.978	1.444	1.632
NH3 Reduction	gms/hr		0.420	-0.045	-0.014

CLAIMS:

1.   A process for making acrylonitrile by reacting propylene with ammonia and oxygen in a fluidized bed of ammoxidation catalyst said process being characterized by introducing vaporized methanol into the reactor under non-coking conditions at a point and in an amount selected such that the ammonia content of the reactor effluent is less than 0.5 mole percent and is lower than that obtained in a comparable process in which no methanol is introduced and that the acrylonitrile production is at least 97 weight percent of that obtained in a comparable process in which no methanol is introduced, an inert gas being introduced with the methanol such that total linear gas flow velocity through the orifices of the methanol introduction means exceeds the linear velocity of flow of other gases through the reactor.

2.   The process of claim 1 wherein the linear velocity of gas flow through the orifices of the methanol introduction means exceeds the linear velocity of flow of other gases through the reactor by ten to thirty times.

3. The process of claim 2 in which the ammonia content of the effluent is less than 0.25 mole percent.

4. The process of claim 2 wherein acrylonitrile production is at least 99 weight percent of that obtained in a comparable process in which no methanol is introduced.

5. The process of claim 1 in which the methanol is mixed with at least 20 mole percent steam or air or mixture thereof.

6.   The process of claim 5 in which the methanol is mixed with at least 20 mole percent steam.

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7.   The process of claim 6 wherein the amount of methanol introduced is controlled such that the methanol content of the effluent is less than 0.25 mole percent.

5   8.   The process of claim 7 wherein the methanol content of the effluent is less than 0.01 mole percent.

9.   The process of claim 5 wherein from 5 to 60 weight percent of the fluidized catalyst in the

10   fluid bed reactor is above the methanol injection point.

10.   The process of claim 1 wherein the orifices through which methanol is introduced are downwardly oriented and have least dimensions at least

15   ten times larger than the mean particle size of the largest 10 percent by weight of the catalyst in the reactor.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6   C07C253/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 638 546 (STANDARD OIL CO OHIO) 15 February 1995 see claims; examples ---	1-10
X	US,A,5 288 473 (SHAW WILFRID G ET AL) 22 February 1994 see claims; examples ---	1-10
A	US,A,3 911 089 (SHIRAISHI TATSUO ET AL) 7 October 1975 see column 4, line 36 - line 49 -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 June 1996	25.06.96

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Pauwels, G

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